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An oriented built-in electric field induced by cobalt surface gradient diffused doping in $MgIn_2S_4$ for enhanced photocatalytic CH_4 evolution

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1. Experimental Details

1.1 Preparation of the photocatalyst.

All the chemicals used in this experiment, including $MgCl_2 \cdot 6H_2O$, $InCl_3 \cdot 4H_2O$, thioacetamide (TAA) and $Co(NO_3)_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals used mentioned above were of analytical grade and used without further purification.

Synthesis of the $MgIn_2S_4$. $MgIn_2S_4$ was synthesized via a facile hydrothermal method. In a typical synthesis, $MgCl_2 \cdot 6H_2O$, $InCl_3 \cdot 4H_2O$ and thioacetamide (TAA) were dissolved in 30 mL deionized water. After 30 min magnetic stirring, the resulting heterogeneous solution was transferred into a 50 ml Teflon-lined stainless-steel autoclave and maintained at 120 °C for 24 h in an oven. After natural cooling, the red precipitate was collected by centrifugation, rinsed alternately with distilled water and ethanol, and then dried at 60 °C for 10 h.

Synthesis of Co-doped $MgIn_2S_4$. In a typical synthesis, the as-prepared $MgIn_2S_4$ was ultrasonically dispersed into 20 ml of deionized water. Then, a calculated amount of $Co(NO_3)_2 \cdot 6H_2O$ was added into the $MgIn_2S_4$ suspension. After 30 min magnetic stirring, the resultant suspension was transferred into a 50ml Teflon-lined stainless-steel autoclave and heated at 120 °C for 24 h. After natural cooling, the product was collected by centrifugation, rinsed alternately with distilled water and ethanol, and then dried at 60 °C for 10 h. For the convenient reason, the as-obtained samples with $Co(NO_3)_2 \cdot 6H_2O/MgIn_2S_4$ molar ratios of 10%, 20%, 40%, 60%, and 80% were marked as $MgIn_2S_4$-Co1, $MgIn_2S_4$-Co2, $MgIn_2S_4$-Co3, $MgIn_2S_4$-Co4, and $MgIn_2S_4$-Co5, respectively.

1.2 Characterization.

X-ray powder diffraction (XRD) were evaluated by a Bruker D8 focus with Cu Kα radiation (40 kV/40 mA). X-ray photoelectron spectroscopy (XPS) was identified on an ESCALAB 250xi (ThermoFsher, England) electron spectrometer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was conducted on Hitachi S-4800 and JEM-2100, respectively. UV-vis diffuse reflectance spectra (DRS) were carried out by a Varian Cary 5000 UV-vis spectrophotometer. The luminescence decay curve was performed on a spectrofluorometer (HORIBA, JOBIN YVON FL3-21). All the measurements were measured at room temperature.

1.3 Photocatalytic activity.

The photocatalytic activities of as-obtained samples were tested by the photocatalytic CO_2 reduction experiment. 10 mg photocatalyst was evenly dispersed on a watch glass with an area of about 28 cm^2. 1.7 g $NaHCO_3$ was put into the reaction cell, and then the reaction was vacuum-treated. Prior to light irradiation, Subsequently, 15 mL H_2SO_4 aqueous solution (4 M) was injected into the vacuum reactor to react with $NaHCO_3$ to get 1 atm CO_2 gas (1 atm). The H_2O vapor, which was the source of the H in CH_4, was produced by the reaction between $NaHCO_3$ and H_2SO_4 and evaporated from H_2SO_4 aqueous solution. A 300 W Xe arc lamp with a UV-cutoff filter ($\lambda \geq 420$ nm) was used as a light source and positioned 5 cm above the photocatalytic reactor. The light intensity was approximately 430 $mW\cdot cm^{-2}$. At given time intervals, 1 mL resulting gas was collected and then qualitatively analyzed by a GC 9790II gas chromatograph (Zhejiang Fuli Analytical Instrument Co., Ltd., China) equipped with a GDX502 flame ionization detector and a TDX-01 thermal conductivity detector. To determine the source of the carbon in the product, isotopic experiments were conducted under the same conditions using $^{13}CO_2$ (purity: 99%) instead of $^{12}CO_2$ (produced by the reaction between $NaHCO_3$ and H_2SO_4), and the CH_4 evolution was analyzed by gas chromatography-mass spectrometry (GC-MS). To evaluate the stability, $MgIn_2S_4$-Co2 sample taken as a model was reevaluated in the light of the aforementioned procedure.

1.4 Photoelectrochemical measurement.

The photoelectrochemical measurements, including electrochemical impedance spectra (EIS) and Mott-Schottky curve, were conducted on an electrochemical analyzer (CHI660E, Shanghai) equipped with a standard three-electrode system. Ag/AgCl (saturated KCl) and platinum (Pt) wire were used as reference electrode and the counter electrode, respectively. A 300W Xe arc lamp with a UV light cut off filter ($\lambda \geq 420$ nm) was taken as light source. The electrolyte solution was 0.35 M Na_2SO_3 and 0.25 M Na_2S aqueous solution. To prepare the working electrodes, 10 mg of sample was dispersed in 800 μl ethanol. Subsequently, the obtained suspension liquid was dropcoated on a ITO glass with size of 20 mm × 40 mm, and dried at 60 ℃ for 10 h in the air.

1.5 Density functional theory (DFT) calculations.

The present first principle DFT calculations were performed by Vienna Ab initio Simulation Package(VASP)[1] with the projector augmented wave (PAW) method.[2] The exchange-functional was treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[3] functional. The valence electron configurations applied in this work were $2s^22p^2$ (C), $2s^22p^4$ (O), $3s^2$ (Mg), $3s^23p^6$ (S), $4d^{10}5s^25p^1$(In) and $3d^84s^1$(Co), respectively. The energy cutoff for the plane wave basis expansion was set to 400 eV and the force on each atom less than 0.03 eV/Å was set for convergence criterion of geometry relaxation. The supercell was constructed by a two-layer 2 × 2 $MgIn_2S_4$ (001) slab and a 20 Å vacuum, in order to avoid the interaction between periodic structures, and the bottom four layers of atoms were fixed. Due to the huge number of atoms containing in the slab model (near 150 atoms), a 1 × 1 × 1 Monkhorst and Pack k-point sampling was employed through all the computational process.[4] The self-consistent calculations apply a convergence energy threshold of 10^{-4} eV. Considering that Co^{2+} and Mg^{2+} have the same valence state and close ion radius (the radius for Co^{2+} and Mg^{2+} are 0.075 nm and 0.072 nm), we modeled the Co doped $MgIn_2S_4$ structure by substituting the Mg atom with Co.

The rate-determining step of CO_2 photocatalytic reduction reaction is: $*CO_2 + H^+ + e^- \rightarrow *COOH$.[5] Here, the asterisk (*) represents the surface substrate active site. The free energies of the $*CO_2 \rightarrow *COOH$ steps was calculated by the equation:[6] $\Delta G = \Delta EDFT + \Delta EZPE - T\Delta S$, where ΔEDFT is the DFT electronic energy difference of each step, ΔEZPE and ΔS are the correction of zero-point energy and the variation of entropy, respectively, which are obtained by vibration analysis, T is the temperature (T = 300 K).

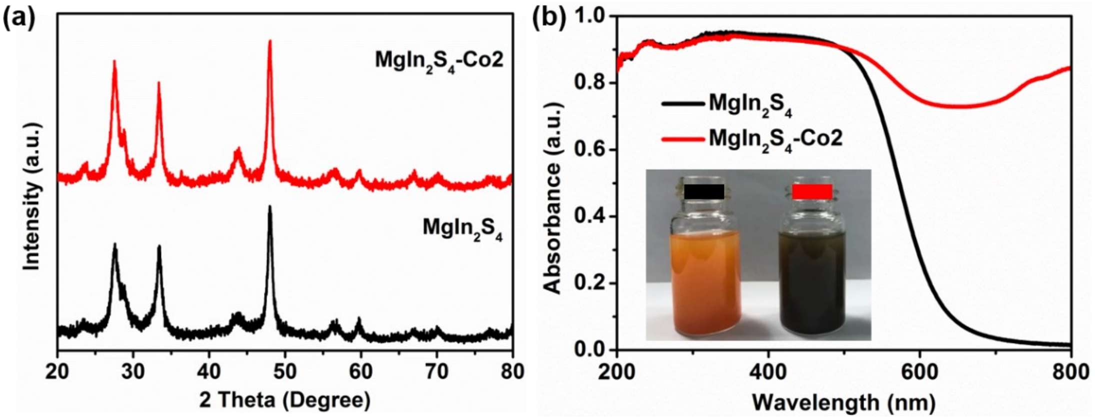

Figure S1. XRD patterns (a), DRS spectra and digital photo of suspensions in the inset (b) of $MgIn_2S_4$ and $MgIn_2S_4$-Co2 samples.

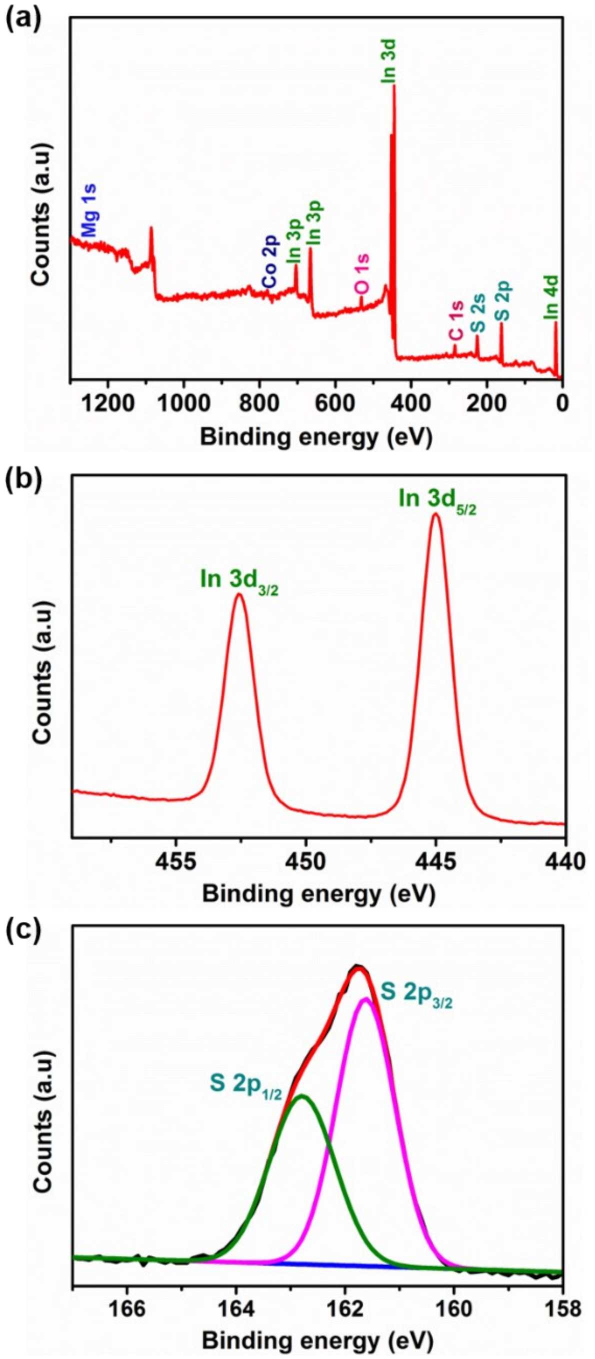

Figure S2. Typical XPS survey spectra (a), high-resolution XPS spectra of In (b) and S (c) for $MgIn_2S_4$-Co2 sample.

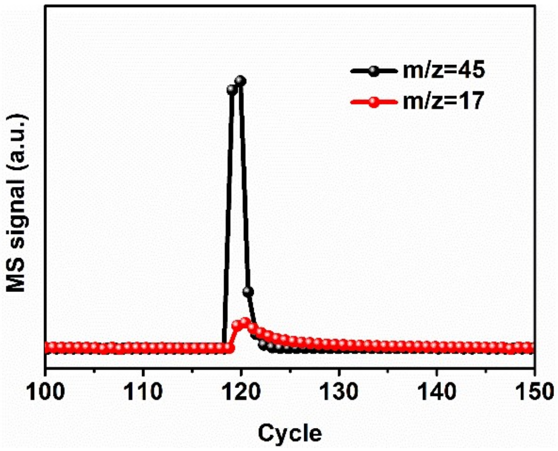

Figure S3. Typical mass spectra for CO_2 reduction over $MgIn_2S_4$-Co2 sample under $^{13}CO_2$ atmosphere.

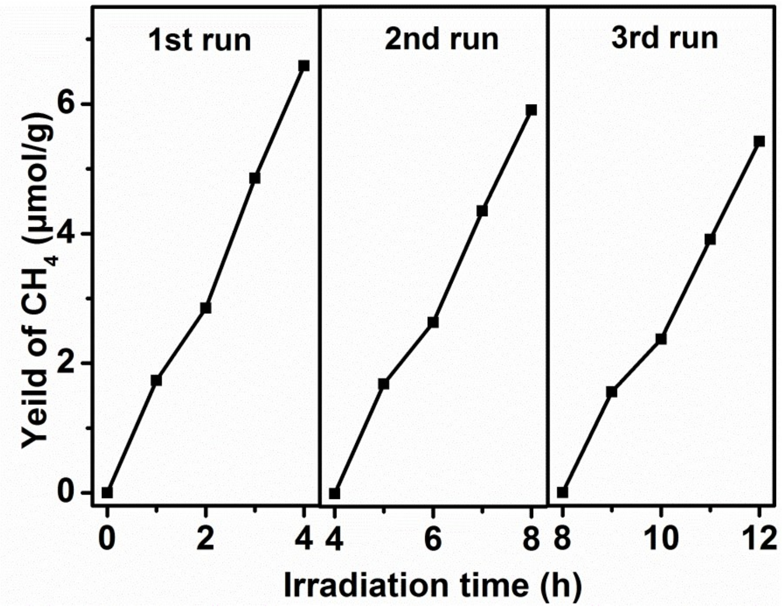

Figure S4. Cycling runs for CO_2 reduction of $MgIn_2S_4$-Co2 sample.

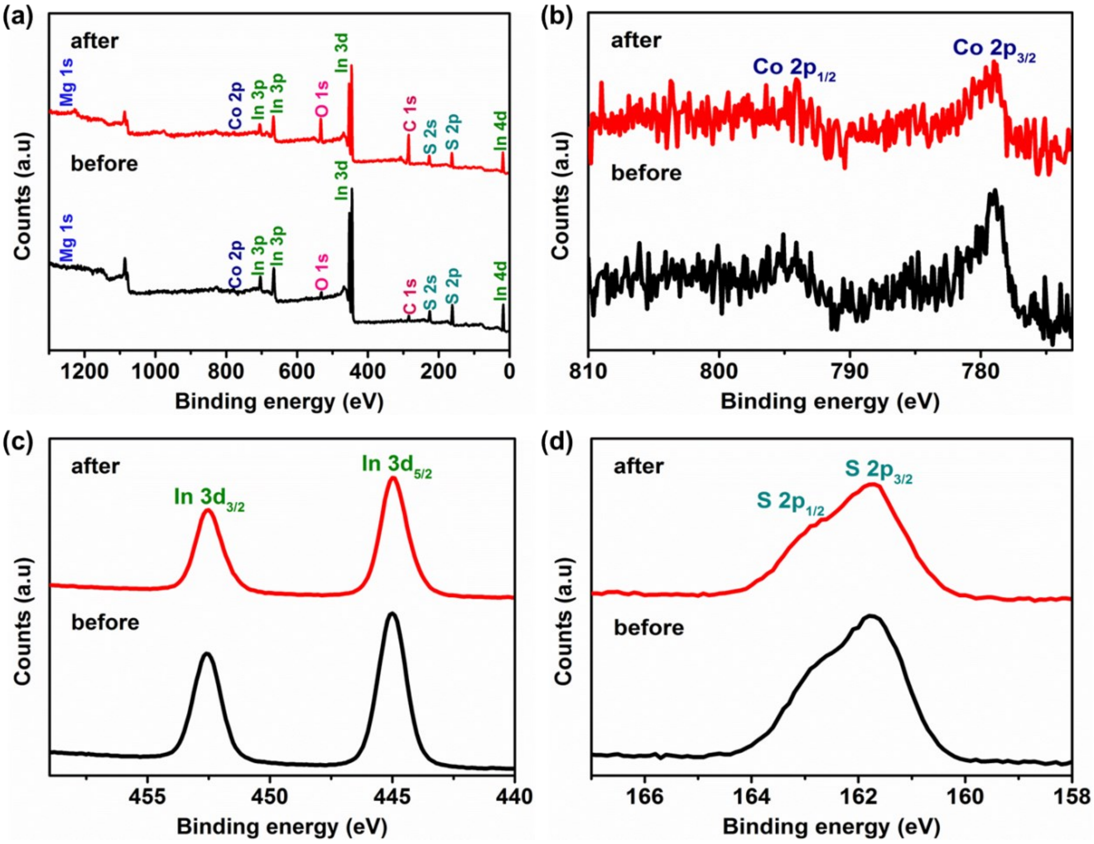

Figure S5. Typical XPS survey spectra **(a)**, high-resolution XPS spectra of Co **(b)**, In **(c)**, and S **(d)**, for $MgIn_2S_4$-Co2 sample before and after photocatalytic reaction.

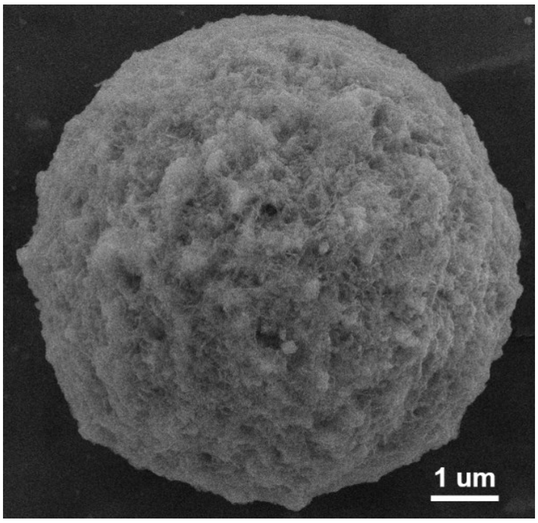

Figure S6. SEM image of $MgIn_2S_4$-Co2 sample after photocatalytic reaction.

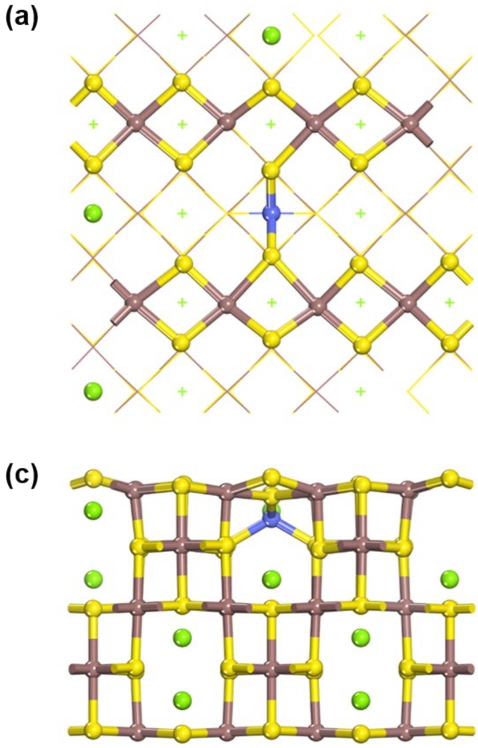

Figure S7. Top view and side view of model structure for Co doped $MgIn_2S_4$ (001). The green, brown, yellow and blue atoms stand for Mg, In, S and Co atoms, respectively.

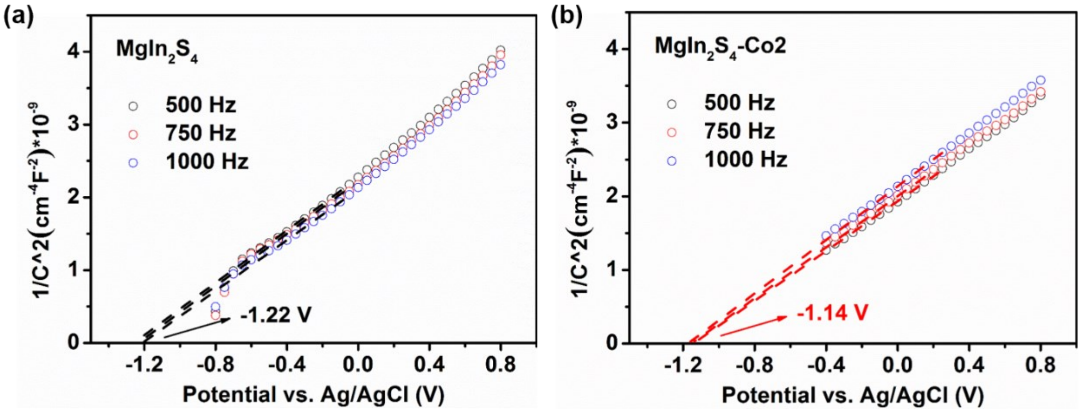

Figure S8. Mot-Schottky curves conducted under different frequencies for $MgIn_2S_4$ (a) and $MgIn_2S_4$-Co2 (b) samples.

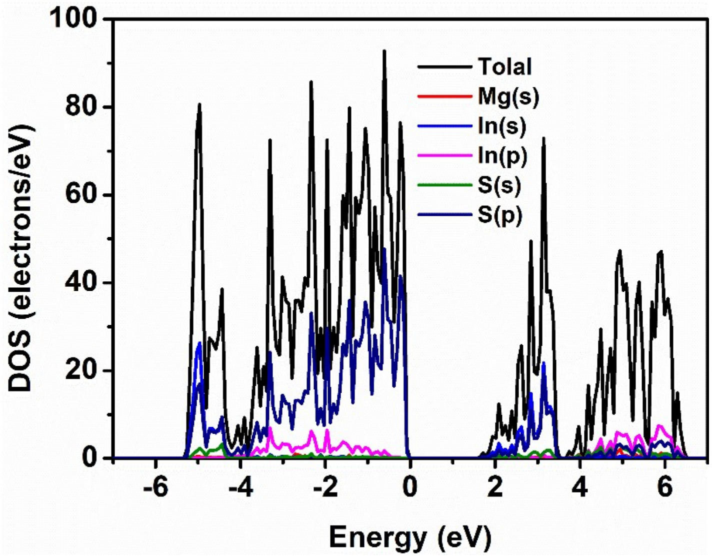

Figure S9. Density of state of the simulated Co-doped $MgIn_2S_4$ system.

Notes and references

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